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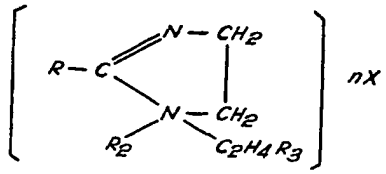
(54) QUATERNARY IMIDAZOLINE DERIVATIVES AND THEIR USE AS SURFACE ACTIVE COMPOUNDS FOR PULP SLURRY

(71) We, HONSHU PAPER COMPANY LIMITED, a corporation duly organized under the laws of Japan and existing at No. 12—8, Ginza 5-chome, Chuo-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of fluffy pulp webs suitable for use in sanitary napkins and disposable diapers, more particularly to surface-active compounds which serve to render the finished pulp web product highly resilient and moisture-absorptive.

According to the invention, there is provided a surface-active compound for imparting moisture-absorbance and resilience to pulp web products which comprises an imidazoline derivative having one of the following formulae:

(I)



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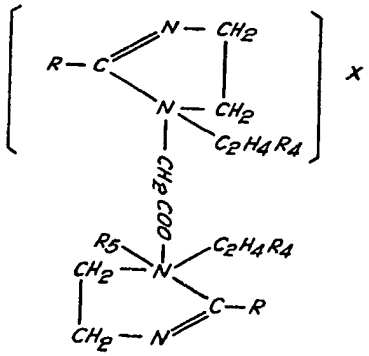

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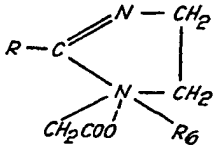
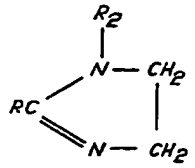


where R is an alkyl or alkenyl group containing 13 to 21 carbon atoms;
R_2 is $-CH_3$, $-C_2H_5$, $-C_2H_4OH$ or $-C_3H_6OH$;
R_3 is —OH, —NHOCR (R is the same as above) or



(R and R_2 are the same as above);
R_4 is —OH or —NHOCR (R is the same as above);
R_5 is $-C_2H_4OH$ or $-C_3H_6OH$;
R_6 is the same as R_5 or $C_2H_4OCH_2COONa$;
X is a halogen atom, $-NO_3$, $-CH_3SO_4$ or $-C_2H_5SO_4$; and
n is an integer of 1 or 2.

There have hitherto been proposed various methods for the manufacture of pulp webs or sheets adaptable for the abovementioned sanitary products. A typical method is known in the art wherein a wet woodpulp slurry is felted or otherwise formed into a sheet which is disintegrated into filamentary individiual fibres, and the thus disintegrated fibres are formed into a web on an air-lay machine. In order to facilitate the disintegration process as well as to impart suitable resiliency to the pulp web, it has been proposed to add certain surface-active agents to a starting wet pulp slurry as disclosed in Japanese Patent Publication Nos. 41—9801 and 44—24682. Such methods, however, are not entirely satisfactory in that it is not possible thereby to produce pulp webs having the desired properties of resiliency and moisture-absorbency both at the same time, as later explained.

The method disclosed in Japanese Patent Publication No. 41—9801 is directed to the use of anion-type or nonion-type surface-active agents; however, these surfactants cannot exhibit the desired performance comparable to cation-type surfactants unless they are used in exceedingly large amounts. Japanese Patent Publication No. 44—24682 teaches the use of cation-type surfactants which are very effective for relatively small amounts in rendering the pulp web resilient; however, such surfactants tend to impart to the pulp web a repellency to water, hence less moisture-absorbency.

For purposes of illustration, some typical surface-active compounds known in the prior are were tested for their performance of imparting water (moisture) absorbency and resiliency to pulp webs according to the following.

Testing procedure.

Bleached sulfate pulp was defibrated at 20°C for 90 seconds and made into slurry of 2% pulp consistency, followed by addition of water to dilute the slurry to 0.5% pulp consistency. To the dilute slurry was added a predetermined amount of each of the various sample surfactants as 10% solution, and the admixture was stirred for about 1 minute. It was thereafter processed by a console-type paper-making machine into a pulp sheet of 230 g/m² which was pressed at a pressure of 2 kg/cm² for 2 minutes and then dried at 140°C for 5 minutes. Each of the resulting pulp sheet weighing 5 grams was crumpled into a ball and placed in a wire mesh cylinder of 50 mm in diameter and 80 mm in length, and dropped into water of 25°C from a height 1 cm above the water surface. The time required for the test sample to submerge completely was measured thereby determining its absorbing ability. The test of resiliency was performed by hand feel to determine how resiliently each sample yields.

The results of the above tests are shown in the following Table.

TABLE 1

Samples of prior-art surfactants	Type of ion	Amount % based on total pulp weight	Water-absorbency (sec.)	Resiliency
Octadecyldimethylammonium chloride	cation	2	60 or above	excellent
Dilauryldimethylammonium chloride	,,	2	35.0	fair
Tridecyldimethylammonium chloride	,,	2	60 or above	fair
Di-(hydrogenated tallow)-dimethyl-ammonium chloride	,,	2	,,	excellent
Sodium oleate	anion	2	6.2	poor
Sodium oleylsulfate	,,	2	1.9	poor
Same as above	,,	6	1.5	fair
10 mol ethylene oxide adduct of palmityl alcohol	nonion	2	1.7	poor
Same as above	,,	6	1.6	poor
Blank	–	–	2.4	–

The above tabulated data indicates that none of the prior-art cation surfactants can impart sufficient water (moisture) absorbency or resiliency to the pulp web. Experiments further indicate that these cation surfactants tend to give srong irritation to the skin. The anion or nonion type surfactants have been found virtually ineffective for imparting the resilient property to the pulp web.

Accordingly, it is the primary object of the present invention to provide surface-active compounds which exhibit a remarkable performance in imparting to pulp webs both water absorbing and mechanically resilient properties.

It is another object of the invention to provide a method of producing fluffy pulp webs in the form of cotton-like sheet materials which are water-absorptive and resilient

to suit, for example, the application for sanitary napkins, disposable diapers and nursing pads.

The surface-active compounds according to the invention are either cationic or amphoteric and have the particular characteristics represented by the formulae I to III given above.

The surface-active compounds of Formula (I) may be produced for instance by subjecting higher fatty acids to dehydro-condensation reaction with ethylene diamine, hydroxyethylethylene diamine or triethylene tetramine at a temperature of from 160°C to 250°C thereby forming an imidazoline compound which is further reacted with methylchloride, methylbromide, nitric acid, chloric acid or diethyl sulfate to render the nitrogen quaternery in the imidazoline ring. It will be understood that with nitric acid and chloric acid, the addition of ethylene oxide or propylene oxide is required to quaternerise the nitrogen in the imidazoline ring.

The compounds of Formula (II) may be produced by reacting the imidazoline compounds formed as above with monochloroacetic acid or monobromoacetic acid, followed by the addition of ethylene oxide or propylene oxide to thereby quaternerize the nitrogen in the imidazoline ring.

The compounds of Formula (III) may be easily obtained by reacting the above imidazoline compounds with sodium monochloroacetate, sodium monobromoacetate, caustic soda or caustic potash.

Certain specific surface-active compounds of the above are given in the following Example which is provided for a better understanding of the invention.

The surface-active compounds of the invention are characteristically different from and superior in the intended performance to any previously known surfactants in that only appreciable amounts, say about 0.1—3 weight percent based on total pulp weight, are sufficient to render the pulp web product appropriately resilient and flexible and further in that the surfactants of the invention are free from impairing the moisture-absorbing property peculiar to pulp and hence help retain this property in the product. Another advantage of the surfactants of the invention is that they give an absolute minimum of irritating or otherwise objectionable stimulating feel to the skin, so that they may be particularly useful for pulp web products such as sanitary napkins and disposable diapers.

Advantageously, the surface-active compounds according to the invention can be used alone with satisfactory results but may be blended with other nonionic surfactants such as polyoxyethylene alkylether and polyethyleneglycol fatty acid where increased moisture-absorbency is desired.

It is to be noted that the compounds of Formulae (I) and (II) above are normally 4 to 6 in pH value as a solution and hence can be readily applied to pulp slurry. However, a compound of Formula (III) in the state of a solution has a pH value of 7 to 6 and should therefore be added with suitable acids to adjust its pH to the range of 4 to 6 to obtain a maximum effect.

The invention will now be described by way of the following Example which is only illustrative and should not be construed as limiting the invention.

CONSOLIDATED EXAMPLE.

Bleached sulfate pulp slurry of 2% pulp consistency was subjected to defibration in a console-type defibrator at 20°C for 90 seconds, followed by dilution with water to bring the pulp consistency to 0.5%. To the pulp slurry was added a predetermined amount of 10% solution of each of the different surface-active compounds listed below. The admixture was stirred with a glass rod for about 1 minute and thereafter formed into a sheet weighing 230 g/m² by a console-type paper-making machine. The resulting sheet was pressed at 2 kg/cm² for 2 minutes, followed by drying at 140°C for 5 minutes. The pulp sheet thus obtained was tested for water-absorbency and resiliency according to the procedure employed in connection with Table 1 above. Breaking length tests were also made of each of the pulp sheets obtained in this Example in accordance with the formula given below.

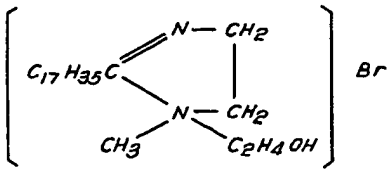
$$\text{Breaking length (km)} = \frac{\text{Tensile strength}^* \text{ (kg)} \times 1000}{\text{Weight of sheet (kg/m}^2\text{)} \times \text{width of sheet (mm)}}$$

*Measured at a temperature of 20°C and a relative humidity of 65%.

The compounds employed in the above Example are as follows:

Specific Surface-Active Compounds.

(A)



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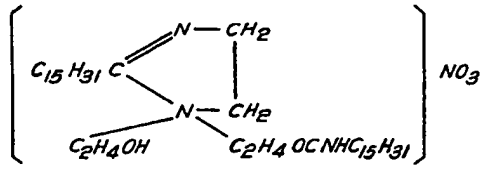

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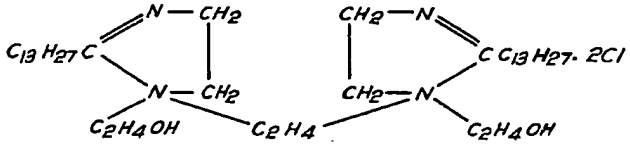

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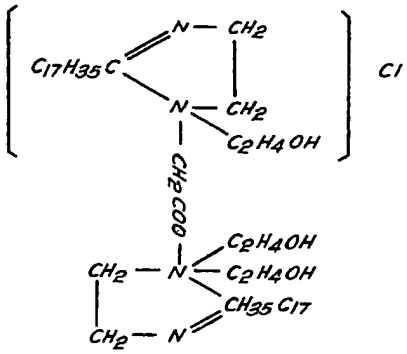
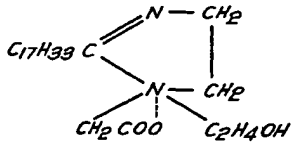
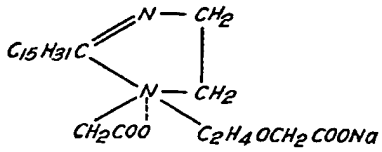


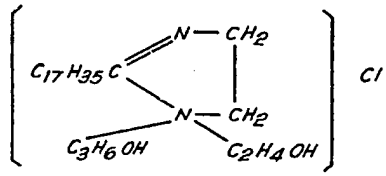
(E)



(F)



(G)



Test data on the various sample pulp webs prepared according t the invention are shown in Table 2 below.

TABLE 2

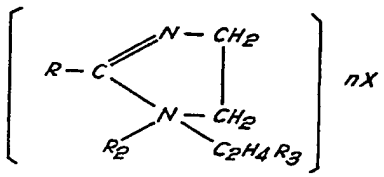
Samples of Inventive Surface-Active compounds	Amount % based on total pulp weight	Water-absorbency (sec.)	Resiliency	Breaking length (km)
A	1	3.2	Excellent	0.28
B	1	5.8	,,	0.33
C	2	1.6	,,	0.27
D	1	4.5	,,	0.34
E*	1	6.0	,,	.0.32
F*	2	3.4	,,	0.29
G	1	5.2	,,	0.35
Blank	—	5.6	—	0.71

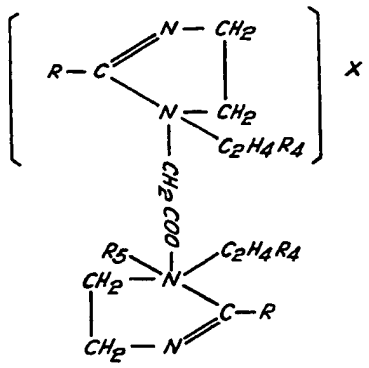
*Samples E and F were adjusted in pH to 5.0 with added chloric acid.

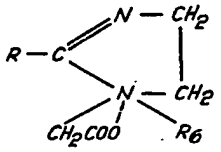
Additional tests were made with respect to the effect of skin irritation, wherein 720 milliliters water containing 1 gram of each of the above sample compositions dissolved therein was applied to rabbits. More specifically, five droplets of the solution were applied to one ear of each of three rabbits over an area of 5 cm^2 by 7 cm^2 once each day, with ethanol similarly applied to the other ear of each rabbit. This experiment was repeated for 14 consecutive days, with the results that none of the rabbits showed any sign of abnormalities. In contrast, similar experiments were conducted with use of octadecyldimethyl ammonium chloride, tridecyldimethyl ammonium chloride and di-(hydrogenated tallow)-dimethyl ammonium chloride, whereby each rabbit showed evident abnormalities.

WHAT WE CLAIM IS:—

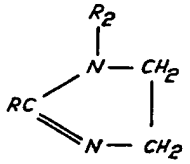
1. A surface-active compound suitable for imparting moisture-absorbence and resilience to pulp web products comprising an imidazoline derivative having one of the following formulae:

(I) 

(II) 

(III) 

where R is an alkyl or alkenyl group containing 13 to 21 carbon atoms;
R_2 is $-CH_3$, $-C_2H_5$, $-C_2H_4OH$ or $-C_3H_6OH$;
R_3 is —OH, —NHOCR (R is the same as above) or



(R and R_2 are the same as above);
R_4 is —OH or —NHOCR (R is the same as above);
R_5 is $-C_2H_4OH$ or $-C_3H_6OH$;
R_6 is the same as R_5 or $C_2H_4OCH_2COONa$;
X is a halogen atom, $-NO_3$, $-CH_3SO_4$ or $-C_2H_5SO_4$; and
n is an integer of 1 or 2.

2. A method for producing fluffy pulp webs or sheets suitable for use as sanitary napkins and disposable diapers which comprises forming wet woodpulp slurry into a sheet and disintegrating said sheet into individual filamentary fibre, characterised in that 0.1 to 3% by weight of a compound as claimed in claim 1 based on total pulp weight is added to said pulp slurry thereby imparting both moisture-absorbency and resiliency to the pulp web.

3. A compound as claimed in claim 1 and having a pH value of 4 to 6.

4. A method as claimed in claim 2 and substantially as herein described with reference to the specific embodiments.

5. A compound according to claim 1 and substantially as herein described with reference to the specific embodiments.

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